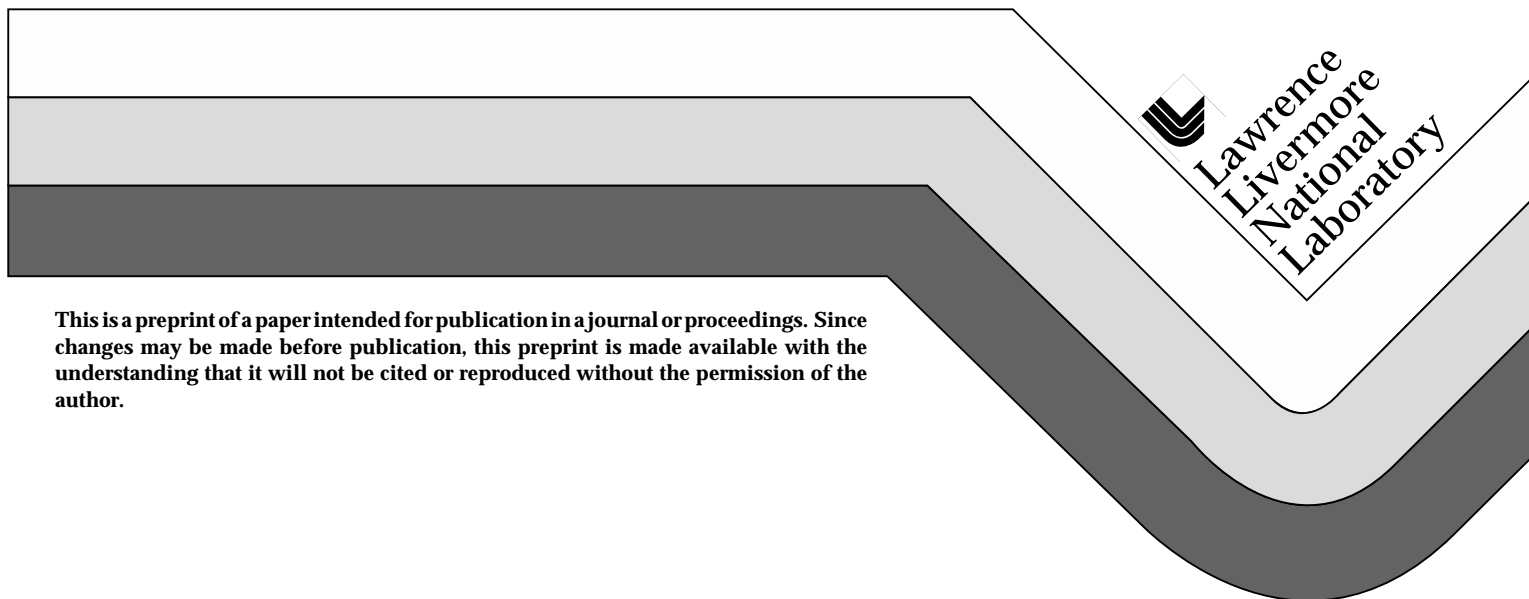


Laser Isotope Purification of Lead for Use in Semiconductor Chip Interconnects

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Laser Isotope Purification of Lead for Use in Semiconductor Chip Interconnects

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Abstract

Lead, used throughout the electronics industries, typically contains small amounts of radioactive ^{210}Pb (a daughter product of the planet's ubiquitous ^{238}U) whose ^{210}Po daughter emits an α -particle that is known to cause soft errors in electronic circuits. The ^{210}Pb is not separable by chemical means. This paper describes the generic Atomic Vapor Laser Isotope Separation (AVLIS) process developed at the Lawrence Livermore National Laboratory (LLNL) over the last 20 years, with particular emphasis on recent efforts to develop the process physics and component technologies required to remove the offending ^{210}Pb using lasers. We have constructed a developmental facility that includes a process laser development area and a test bed for the vaporizer and ion and product collectors. We will be testing much of the equipment and demonstrating pilot-scale AVLIS on a surrogate material later this year. Detection of the very low alpha emission even from commercially available low-alpha lead is challenging. LLNL's detection capabilities will be described. The goal of the development of lead purification technology is to demonstrate the capability in FY97, and to deploy a production machine capable of up to several MT/y of isotopically purified material, possibly beginning in FY98.

Introduction

It has been known^{1, 2, 3, 4, 5} that soft errors (random, non-recurring errors) can be caused by alpha particle radiation. The source of the radiation was identified to be uranium, thorium, and ^{210}Po which are all removable to acceptable levels by chemical means. The ^{210}Po , however, results from the radioactive decay of ^{210}Pb (by two beta emissions) which is present in the ubiquitous lead used to bond interconnects. The ^{210}Pb cannot be removed by chemical means and so will remain as a source of ^{210}Po , and the alpha emissions. Because of the relatively short half life of ^{210}Pb compared to ^{238}U , the specific activity of the former is about 2×10^8 times greater than the later. Thus, the soft errors associated with 2 ppm of uranium is equivalent to 1×10^{-8} ppm of ^{210}Pb . Over the last

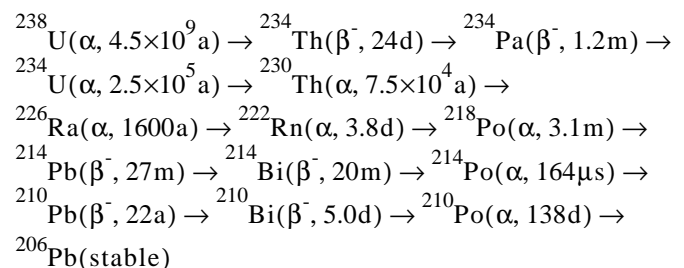
25 years the electronics industry has reduced the alpha emitters from the packaging materials, and have found naturally occurring and other sources of low-activity lead. Because ^{210}Pb has a 22.3 year half life, some of the sources have come from century-old ship ballast, plumbing, etc. In nature there occurs large variations in the concentration⁶ of ^{210}Pb , from as high as (in terms of surface activity) 70 counts/cm²/h to as low as 0.01 counts/cm²/h.

For the present-day devices (0.35 μ feature size) the lowest activity naturally occurring lead is adequate, but for the next generation and beyond an order-of-magnitude reduction will be required. In addition, the 0.01 counts/cm²/h material is in short supply. There is, however, an essentially inexhaustible supply of lead with an activity of 0.05 counts/cm²/h.

In this paper we describe technology under development in our laboratories that, if successful, will be able to economically purify the 0.05 counts/cm²/h material to levels at or below 0.001 counts/cm²/h. Although largely peripheral to the main topics discussed at this conference, this technology is both timely and important for future generations of electronic devices.

α - Particles and Soft Errors

Lead is a key material used in the Controlled Collapsed Chip Connection (C⁴) technique that is used to form connections between the IC chip and the package. One isotope of lead, ^{210}Pb , is radioactive with a half-life of 22.3y, formed as the by-product of uranium decay, and is found in low concentrations in lead ore. The uranium decay chain along with the relevant decay mechanisms and radioactive half lives is shown below⁷.



The alpha emissions that come from the ^{210}Po daughter of ^{210}Pb can cause soft errors at unacceptable rates in the memory or logic circuitry of the integrated chip, and in

1. T. C. May and Murray H. Woods, IEEE Reliability Physics Symposium, 33, 1978.
2. D. P. Bouldin, J. Electronic Materials, **10**, 747, 1981.
3. S. C. Liang, J. Vac. Sci. Technol. **B 2**, 714, 1984.
4. John A. Dunlop, Keith E. Ritala, James R. Gibbard, Ron Beauprie, Benoit Pouliquen, James H. Reeves, John C. Huneke, and Wojciech A. Vieth, JOM, 18, June, 1989.
5. Timothy J. Gorman, IEEE Trans. Elec. Dev. **41**, 553, 1994.

6. The variation of ^{210}Pb in lead ore has a long history in radiation detectors. See in particular, R. L. Weller, Health Physics **41**, pg. 15, 1981.
7. "Nuclides and Isotopes", 14th Ed., General Electric Company, 1989.

particular, in C4 devices because of the close proximity of the lead bumps to the logic circuitry. This may place limitations on C4 usefulness or impose design constraints in future generations of ICs, particularly as reductions in feature size, capacitance, and operating voltage increase sensitivity to alpha emissions.

History of the AVLIS Program at LLNL

The AVLIS Program at LLNL is developing a capability of isotopically purifying lead for these applications by applying our uranium isotope separation technology. Over the past 20 years AVLIS has developed a laser-based method for separating isotopes^{8, 9, 10, 11}. As shown schematically in Fig. 1,

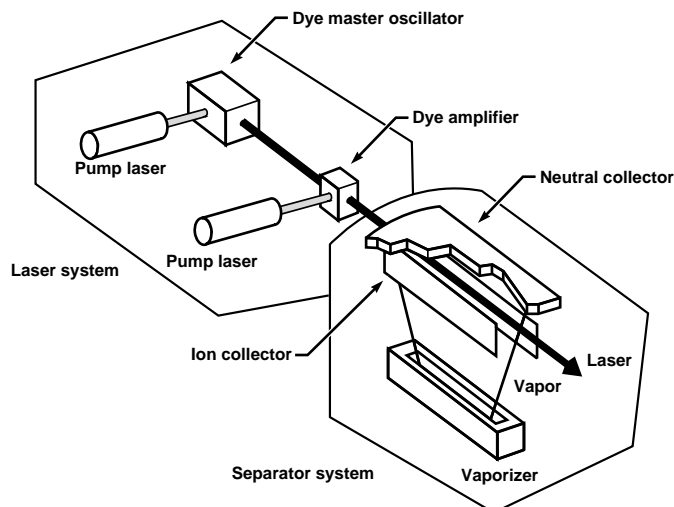


Fig. 1. Schematic of major subsystems employed in the AVLIS process.

an element is heated within a vacuum vessel with either an electron beam or, in the case of more volatile materials, resistive heater. Material vaporizes and streams upward forming a low density atomic vapor. This vapor is illuminated with multiple laser wavelengths and is step-wise resonantly excited until it has enough energy to ionize. The lasers are set at precisely controlled frequencies and have sufficiently narrow frequency bandwidth to ionize a single isotope, in this case ^{210}Pb . The resulting isotopically-enriched plasma, formed between pairs of charged extractors, is electrostatically separated and condensed. This “waste” material is enriched in the isotope selected by the laser and is typically called the Product. The remaining “depleted” neutral vapor stream, called the Tails stream, is condensed on the Neutral collector. This general method of separation of a Feed stream into an

enriched Product stream and a depleted Tails stream is called AVLIS.

The focus of the AVLIS program has been the enrichment of uranium for use in commercial nuclear reactors. It is from the uranium program that the technical base was built that allows the development program for lead purification to proceed. A cut-away of our enrichment facility is shown in Fig. 2. Plant scale component technologies have been

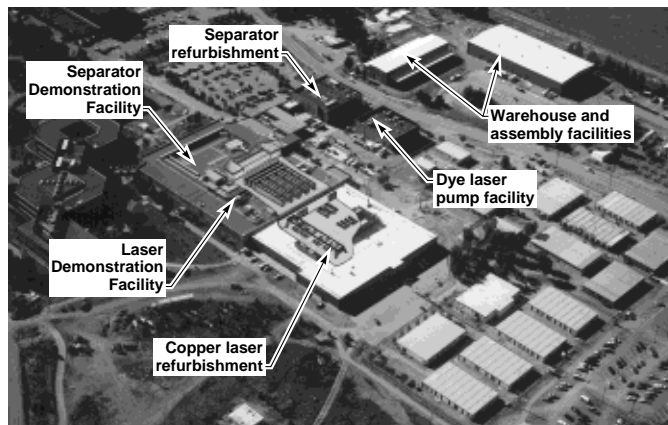


Fig. 2. The uranium enrichment facility at LLNL. The lead purification developmental laboratories are located in the main building.

demonstrated, including copper lasers and refurbishment, dye lasers, separators and refurbishment, and integrated system controls. Shown in Fig. 3 are our copper lasers, which convert



Fig. 3. Two of the modular copper laser chains used for the uranium process. The lead process will use a modular but more compact design.

electrical energy to >10kW of laser light, and have been operated for millions of unit hours. Seen in the figure is the size and scale of two of the copper laser chains, each capable of 1.5kW output power. The design is modular to allow efficient laser refurbishment, which is important for the overall system availability of the production hardware. Although the copper pump lasers will not be used, the modularity is being built into the process lasers under development for lead isotopic purification. The lead process lasers will have significantly lower power, size, and cost.

8. J. I. Davis and E. B. Rockowner, “Lasers in Material Processing”, Lawrence Livermore National Laboratory document UCRL-85175, June 1981.
9. R. C. Stern and J. A. Paisner, “Atomic Vapor Laser Isotope Separation”, Lawrence Livermore National Laboratory document UCRL-93584, June 1985.
10. J. A. Paisner and R. W. Solarz in “Laser Spectroscopy and its Applications”, L. J. Radziemski, J. A. Paisner, and R. W. Solarz, eds., Marcel Dekker Inc., 1987.
11. J. A. Paisner, Appl. Phys. **B 46**, pg. 253, 1988.

In Fig. 4 is shown some of our dye lasers, which convert the copper laser light to a precise, narrow-bandwidth wavelength suitable for AVLIS¹². These systems have been

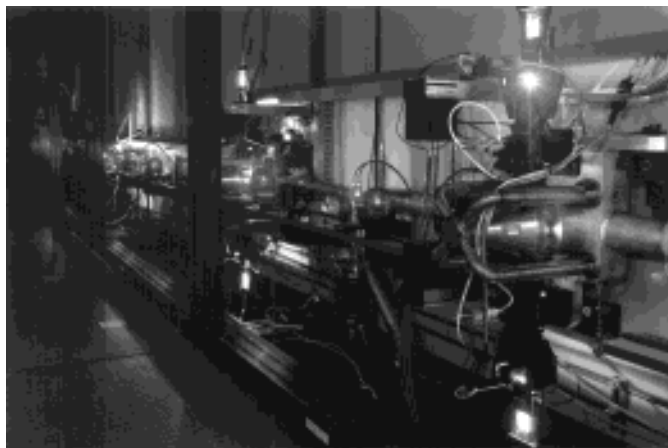


Fig. 4. One of the uranium dye laser chains consisting of a dye master oscillator, followed by several stages of amplification. The dye laser for lead will require fewer amplifiers.

used in round the clock operations in support of enrichment demonstrations, and to gather reliability data.

The separator systems, shown in Fig. 5, have been used to

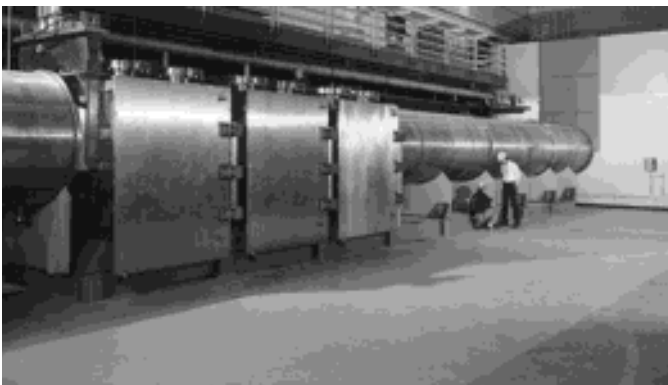


Fig. 5. The uranium separator system at LLNL has been used for both uranium and gadolinium enrichment. The lead separator will be much smaller.

process metric tons of uranium. Integrated demonstrations have produced hundreds of kilograms of reactor grade uranium (enrichments between 2% and 5% ²³⁵U). In addition, the facilities have been used for individual component development and also for the gathering of additional reliability data.

The program has also enriched multi-kilograms of several of the lanthanide series including erbium and gadolinium¹³ as well as investigated enrichment schemes for a host of other elements.

12. I. L. Bass, R. E. Bonanno, R. P. Hackel, and P. R. Hammond, *Appl. Optics* **33**, 6993, 1992.

13. C. Haynam, B. Comaskey, J. Conway, J. Eggert, J. Glaser, E. Ng, J. Paisner, R. Solarz, and E. Worden, *SPIE* **1859**, 24, 1993.

Present Status of the AVLIS Program

By act of Congress a government corporation named the United States Enrichment Corporation (USEC) was formed and subsequently granted all rights to AVLIS technology previously owned by DOE. USEC has submitted a privatization plan to the President and Congress and expects approval this year. The USEC Board of Directors decided in 1994 to take steps toward the deployment of an AVLIS uranium plant. USEC is sponsoring at LLNL the completion of technology development and preliminary uranium plant design in FY96 and FY97.

Under USEC sponsorship, LLNL is also investigating other industrial and medical isotope separation programs for potential future business.

Isotopic Purification of Lead

Initial investigation into lead purification indicates technical and commercial feasibility by application of AVLIS technology developed for the uranium program. Spectroscopic studies have identified photoionization pathways which will efficiently and selectively ionize ²¹⁰Pb. Shown in Fig. 6 is the spectroscopic laboratory used for this work.



Fig. 6. The spectroscopy laboratory used to measure the optical properties of lead needed to specify the process laser requirements.

These studies also provide necessary data to specify the technical requirements of the laser system, and ultimately, the laser costs. For lead purification the required laser system is not available commercially. But by applying expertise gained in the uranium program, we are presently developing a multiple-color prototypical laser system that would be integrated into the purification system. The laser development facility is shown in Fig. 7. This facility will also be usable to support a production system.

The market demand primarily determines the overall dimensions of the separator system, whereas some of the spectroscopic data — isotope shifts, hyperfine splittings, and the like — are required for a specific separator design. In Fig. 8 is shown the separator development facility that is presently

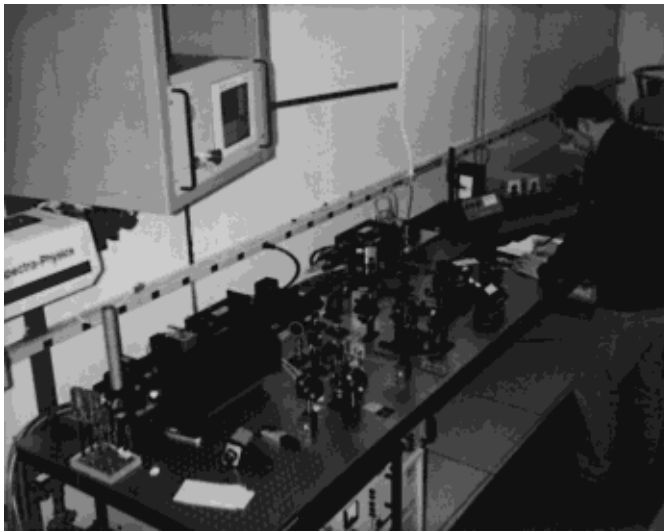


Fig. 7. The facility where the process lasers for lead purification are being developed.

being used to characterize the properties of the atomic lead vapor while varying source designs and design parameters. In



Fig. 8. The developmental separator system where lead vapor properties are being measured. The chamber is on top of a glove box used for lead material handling.

addition to the vapor property measurements, this facility also will be used to develop the Product and Tails collection hardware, and possibly for production at a later time.

This developmental phase is anticipated to extend through the current fiscal year where the prototypical laser and separator hardware required to process lead will be specified and developed. Presuming success and if sufficient commercial interest develops, we will carry out purification demonstrations during the first part of FY97 followed by the development of production-scale hardware later that year and possibly full scale production (MT/y) beginning in FY98.

Success is defined by both the technical merits of the program and the associated costs of the purification. The production costs will be well characterized as part of the development program. The major determining factors are the market size, size of the laser system (i.e. the laser power requirements), the separator cost per unit throughput, and the labor costs required to run the facility.

LLNL's α -detection Capabilities

The Isotope Sciences Division at LLNL routinely measures very low alpha activities of ^{210}Po , a ^{210}Pb granddaughter. A sample solution is spiked with a known amount of ^{209}Po solution (which has been calibrated against a NIST-traceable standard). Spike and sample Po are chemically equilibrated and then spontaneously plated onto a silver planchet. Po activities are determined by alpha energy spectrometry using partially depleted silicon surface barrier detectors. Peak resolution for plated Po is less than 40 keV FWHM, while the energy difference between ^{209}Po and ^{210}Po is greater than 400 keV. The use of a calibrated spike allows quantitative determination of ^{210}Po activity without having to precisely characterize chemical yield, plating efficiency, plating thickness, and counting geometry. For 1–10 grams of industrial lead, the detection limit is better than 0.001 alphas/hour/cm². The only disadvantage to the technique is that in order to relate ^{210}Pb activity to measured ^{210}Po activity, the extent of secular equilibrium between parent and granddaughter must be known. For recently chemically processed samples, a second ^{210}Po determination must be made several months after the first determination. For samples which have not been chemically processed for five half-lives of ^{210}Po (at least two years), secular equilibrium can be assumed, and only a single measurement is required.

LLNL also has beta-counting facilities, and ^{210}Pb can be determined by beta counting its ^{210}Bi daughter. Because ^{210}Bi has a much shorter half-life than ^{210}Po (5 days vs. 138 days), secular equilibrium with ^{210}Pb is established much more rapidly (1 month vs. 2 years). The ^{210}Bi technique involves adding stable Bi to the sample solution as a carrier and yield monitor, chemical separation of Bi from other beta and alpha emitters, and beta counting in a gas-flow proportional counter. Higher backgrounds, poorer energy resolution, and corrections for absorption and scattering make the ^{210}Bi technique less sensitive and less precise than the ^{210}Po technique for determining ^{210}Pb activity. But the faster turnaround time is potentially more suitable for development and process applications.

Conclusions

Over the last two years we have built an R&D facility eventually capable of producing MT/y of isotopically purified lead. Much of the hardware is in place and the rest (both lasers and separators) is being developed. Furthermore, we have completed a spectroscopic investigation that has resulted in purification scheme that can in principle reduce the ^{210}Pb content in lead to an industry-specified arbitrarily low value.

LLNL has alpha detection capabilities of immediate use to the semiconductor industry, and of potential use to characterize the lead that has been purified by the AVLIS process.

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